UNIVERSITY OF PENNSYLVANIA

---

# THE ACTION OF AIR CARBON TETRACHLORIDE VAPOR MIXTURES ON CERTAIN NATURAL AND ARTIFICIAL SULPHIDES AND ON SELENIDES AND A TELLURIDE

K. BRADDOCK-ROGERS

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

PHILADELPHIA
1928

# THE ACTION OF AIR CARBON TETRACHLORIDE VAPOR MIXTURES ON CERTAIN NATURAL AND ARTIFICIAL SULPHIDES AND ON SELENIDES AND A TELLURIDE

---

A THESIS

IN CHEMISTRY

PRESENTED TO THE FACULTY OF THE GRADUATE SCHOOL OF THE UNIVERSITY OF PENNSYLVANIA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

K. BRADDOCK-ROGERS

PHILADELPHIA
1928

## ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. H. S. Lukens under whose direction this investigation was conducted, and to Dr. D. L. Wallace for his encouragement and suggestions.

# THE ACTION OF AIR CARBON TETRACHLORIDE VAPOR MIXTURES ON CERTAIN NATURAL AND ARTIFICIAL SULPHIDES AND ON SELENIDES AND A TELLURIDE

Carbon tetrachloride was first used by Watts and Bell in 1878 for the preparation of several metallic chlorides.[1] While this reagent has been employed in the preparation of a long list of substances, it has seldom been employed for quantitative purposes. The reported applications of carbon tetrachloride to quantitative reactions may be summarized in the following:

Jannasch and Harwood volatilized $B_2O_3$ from boric acid in a current of carbon tetrachloride and methyl alcohol,[2] $V_2O_5$ from ammonium meta-vanadate and $V_2O_5$ from sodium vanadate in a stream of carbon tetrachloride. These investigators applied this reaction to the analysis of vanadinite, endlichite, and carnotite. The vanadium from sodium meta-vanadate was completely removed while the phosphorus in di-sodium phosphate was unaffected when these salts were heated in the vapor of carbon tetrachloride. To quantitatively remove phosphorus and vanadium from a mixture of these salts, four times their weight of sodium chloride was added to them and from this mixture the vanadium and the phosphorus were completely removed at a high temperature.

Jannasch and Jilke removed phosphorus from the phosphates of iron, chromium, uranium, zinc, nickel, cobalt, and manganese with carbon tetrachloride vapor.[3] To prevent the volatilization of the metallic chlorides a plug of glass wool was placed in the decomposition tube.

Camboulives heated a number of minerals in a stream of carbon

[1] J. Ch. Soc. 33; 442 (1878).
[2] J. pr. Chem. 80; 134.
[3] J. pr. Chem. 80; 113.

tetrachloride.[4] Corundum was partially decomposed; wolframite was completely decomposed. The anhydrous silicates were more easily attacked as the silica content lowered. Albite, emerald, orthose, oligoclase, labrodorite, and anorthite lost weight inversely proportional to the silica content. He further made the statement that the hydrated silicates were completely transformed by heating in the vapors of carbon tetrachloride. It is reported in the same paper that the free and combined silica in minerals, iron, oxides, bauxites, clays and sands, etc., may be determined. The action of carbon tetrachloride on cymophane, chromite, columbite, scheelite, spinel and emery was reported.

In this laboratory E. F. Smith decomposed the tungstates of barium and sodium by heating them in a stream of carbon tetrachloride.[5] A similar reaction was carried out on lead metatungstate.[6] Moser and Schmidt used mixtures of carbon dioxide and carbon tetrachloride vapor, and air and carbon tetrachloride vapor to decompose scheelite, to determine the per cent purity of $WO_3$ and to determine $WO_3$ in sodium tungstate and in ammonium tungstate; to separate tungsten from iron, and $WO_3$ from $Fe_2O_3$; and also to test the purity of amorphous tungsten and tungsten wire.[7]

In surveying the literature, it is apparent that all previous work has been confined to studies of the action of the reagent on metals, oxides and acid salts, both natural and artificial. No attention has been given to the application of carbon tetrachloride to the decomposition and analysis of sulphides, and it is the purpose of this paper to show that this reagent may be used efficiently for the rapid decomposition and the analysis of sulphides both natural and artificial. This application met with such success that the method was then applied to selenides and tellurides with very gratifying results.

---

[4] Comp. Rend. 150; 221 (1910).
[5] A Monograph—Sodium Tungstates, July 1924, Phila., Pa.
[6] E. F. Smith, *Chemical News* (London) 135; 113 (1927).
[7] Monats. fur Chem. 47; 313 (1926).

PURIFICATION OF THE REAGENTS

*Ammonium Hydroxide.*—The ordinary ammonium hydroxide of the laboratory was distilled in a pyrex apparatus and the solution (Sp. gr. .94) kept in ceresin bottles.

*Hydrochloric Acid.*—The C. P. sulphate free acid 36–38% was used.

*The Hydrochloric Acid-bromine Mixture.*—Into a Greiner and Friedrichs gas washing bottle were placed 75 ccs. of bromine water and 5 ccs. of bromine.[8] This bottle was connected to a second bottle of the same type containing 60 ccs. of concentrated hydrochloric acid. Air was drawn through this system for four to five minutes at the rate of 1800–2000 ccs. per hour. In this way the bromine vapors were absorbed in the hydrochloric acid with no danger of introducing sulphates or sulfuric acid present in the bromine. As an added precaution barium chloride may be added to the bromine water flask. By varying the time and the rate, any desired concentration of bromine in hydrochloric acid may be obtained.

*Ammonium Carbonate.*—The quantitative reagent, sulfate free, was used.

*Hydrogen Peroxide.*—The hydrogen peroxide of commerce contains sulfates, which must be removed. A liter of hydrogen peroxide proved a convenient working volume and to this barium dioxide was added in excess. The solution should be at room temperature, shaken occasionally and allowed to stand about an hour and a half and then filtered through asbestos. The hydrogen peroxide could be preserved without appreciable loss in strength for several days. For mechanical reasons it was found advisable to remove the excess barium sulphate from the solution, when it was to be used in certain types of absorbers. The portion to be used, just before use, was treated with an excess of ammonium carbonate, allowed to stand four to five minutes with

[8] The absorber used was a slight modification of the original. Cf. Form 1, Fig. 5; Z. anal. Ch. 50; 175 (1911).

occasional shaking, and then filtered through asbestos. The hydrogen peroxide and was ready for use.

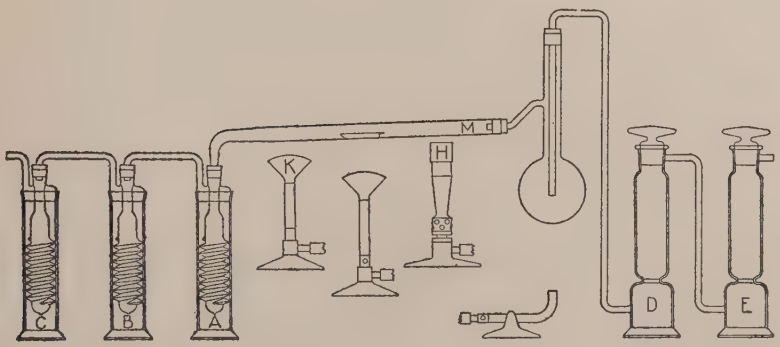
*Carbon Tetrachloride.*—Carbon tetrachloride sold as "sulphur free" was allowed to stand in contact with solid potassium hydroxide for several days and then distilled. The distillate was dried over calcium chloride and again distilled. A test for sulphur was made on this material.

The carbon tetrachloride was heated to 60–65° C. Air free of carbon dioxide and moisture was drawn over it for forty minutes at the rate of 1500 ccs. per hour. The air laden with the vapors of the carbon tetrachloride was heated to 750–800° C. and the resulting gases were absorbed in 75 ccs. of ammoniacal hydrogen peroxide. The hydrogen peroxide was of 3% strength, and purified as described in the preceding paragraph. This sulphate free material was mixed with an equal volume of freshly distilled ammonium hydroxide 0.94 specific gravity. The contents of the absorption flask were washed into a beaker and boiled to expel the excess ammonia, acidulated with hydrochloric acid and tested for sulphates with a solution of barium chloride. A very considerable quantity was found.

The sulphur in the carbon tetrachloride may be easily removed. Three parts of carbon tetrachloride are very vigorously shaken with two parts of 1:1 ammoniacal hydrogen peroxide. This treatment is repeated at least three times with fresh oxidizing material. No definite statement as to the number of times this treatment is to be repeated can be given. The carbon tetrachloride is dried over calcium chloride and distilled and again tested for the presence of sulphur in the manner described. If sulphur is again found to be present, the treatment with the ammoniacal hydrogen peroxide is repeated. No difficulty was experienced in completely and efficiently removing all traces of sulphur compounds.

*Ammoniacal Hydrogen Peroxide.*—Equal volumes of the 3% purified hydrogen peroxide and the distilled ammonium hydroxide 0.94 specific gravity.

## The Apparatus




*A*—Absorber containing hydrochloric acid-bromine mixture.
*B & C*—Absorbers containing ammoniacal hydrogen peroxide.
*D*—Calcium chloride drying tower.
*E*—Potassium hydroxide tower.
*F*—Carbon tetrachloride reservoir, 125 ccs. capacity.
*M*—Clear quartz tube, 38 cm. long and 1.7 cm. bore.
*H*—Portion of tube above burner 5–7 cm. heated at 750–800° C.
*K*—Portion of tube above burner 3–5 cm. heated at 400–450° C.

The towers *D* and *E* washed the air free of moisture and carbon dioxide. The air was drawn through the system by a water aspirator (not shown in the picture) attached to *C*. The air inlet tube of the carbon tetrachloride reservoir should be from one to two cm. above the surface of the liquid. The connections of the absorbing towers were butted together in rubber sleeves.

The absorbers were Greiner and Friedrichs spiral bubbling bottles.

The boats and the tubes were of clear quartz upon which the reacting gases had no effect.

## The General Procedure as Applied to the Analysis of Sulphides

All samples of mineral were ground to pass through a sieve of one hundred meshes to the inch. The sample of mineral was

weighed in a quartz boat and introduced into the center of the decomposition tube.

The air was drawn through the apparatus at the optimum rate of 1500–1700 ccs. per hour, passed over carbon tetrachloride which was kept at a temperature of 40–50° C. The gases passed through the hot portion of the tube over burner *H*, where presumably the following reactions took place:

$$2CCl_4 = C_2Cl_6 + Cl_2$$
$$2CCl_4 = C_2Cl_4 + 2Cl_2$$
$$(C_2Cl_6 = C_2Cl_4 + Cl_2)$$
$$C_2Cl_4 + 2O_2 = 2CO_2 + 2Cl_2$$
$$C_2Cl_6 + 2O_2 = 2CO_2 + 3Cl_2$$
$$2CCl_4 + O_2 = 2COCl_2 + 2Cl_2$$

These gases next passed over the heated mineral in the boat, which is decomposed as follows:

$$RS + 2Cl_2 = S_2Cl_2 + RCl_2$$
$$RS + COCl_2 = COS + RCl_2$$

The heat of 450–500° C. which is applied at *K* prevents the condensation of any volatile chlorides about the end of the boat.

The products of the reaction entered the absorption bottles in which the sulphur compounds were oxidized to sulphates. In the hydrochloric acid-bromine bottle *A*, the sulphur monochloride was oxidized and in *B* and *C* the carbon oxysulphide was oxidized. *C* served largely as a safety trap, as repeated tests showed only traces of sulphates or none at all.

The optimum temperature and other specific conditions to be observed are outlined in the descriptions of the methods that were found best adapted to the decomposition of each particular mineral.

The volatile chlorides in the decomposition tube were united with the contents of the first absorber and the excess bromine and hydrochloric acid expelled by boiling. The contents of the alkaline absorbers were united, boiled to expel the excess ammonia and hydrogen peroxide and evaporated to dryness on the water bath. The residue was then taken up in dilute hydrochloric acid and the solution filtered to remove the silica. (In every case silica was present from the action of the ammonia on the pyrex beakers.) This filtrate and the first acid solution

were united. This solution is hereafter termed the "main solution". The sulphur was precipitated from the main solution as barium sulphate. The treatment of the contents of the boat is described under the detailed analysis of each particular material.

Attempts were made to dispense with the acid absorber and use only ammoniacal hydrogen peroxide. This was successful in the case of sphalerite where the temperature of decomposition was high, but it did not give good results with those substances which decomposed at lower temperatures. The combination of the acid and alkaline oxidizing media fits any case and it is the procedure recommended.

## The Analysis of Natural Sulphides

### *Sphalerite*

The boat and contents were heated for fifteen minutes at 400° C. and then the temperature was raised to 500–550° C. and kept there for twenty to twenty-five minutes. The time of decomposition was forty minutes for a quarter gram sample.

In the analysis of sphalerite two series of experiments were carried out.

In the first series the absorbing and oxidizing agent was ammoniacal hydrogen peroxide in four absorbing bottles. The contents of these four absorbers were washed into a beaker and the solution was evaporated to dryness. The residue was taken up in dilute hydrochloric acid and the silica filtered off. The volatile chlorides in the tube were added to the filtrate. The residue in the boat contained the gangue and traces of zinc chloride. This was leached with water containing a few drops of hydrochloric acid, filtered and added to the filtrate from the main solution, from which the sulphur was precipitated as barium sulphate.

In the second series the four absorbing bottles of ammoniacal hydrogen peroxide were replaced by a chain of three absorbers, the first bottle containing a hydrochloric acid bromine mixture, the second and third bottles, ammoniacal hydrogen peroxide. In every other respect the conditions of the experiment were the same.

SERIES 1

| Weight of Mineral | Weight of $BaSO_4$ | Sulphur |
|---|---|---|
| 0.2078 gm. | 0.3993 gm. | 26.40% |
| 0.2105 gm. | 0.4041 gm. | 26.38% |
| 0.2133 gm. | 0.4088 gm. | 26.33% |
| 0.2115 gm. | 0.4053 gm. | 26.33% |
| Average | | 26.36% |

SERIES 2

| | | |
|---|---|---|
| 0.3250 gm. | 0.6248 gm. | 26.41% |
| 0.3699 gm. | 0.7120 gm. | 26.45% |
| Average | | 26.43% |

Seven analyses, made by other analysts in this laboratory by means of the usual procedure for the estimation of sulphur in minerals, gave an average value of 26.34% sulphur for this sample.

*Pyrite*

The weighed sample of the mineral was warmed for twelve to fifteen minutes so that ferric chloride just formed above the boat, after which the temperature was raised to distill out this volatile chloride. When all of the ferric chloride was sublimed, the temperature was increased to 450–500° C. to sublime the major portion of the copper if the sample contained this element, and to convert to the chlorides any oxide of iron which might have formed. The total time required for the decomposition was thirty-five to forty minutes for a three-tenths gram sample. When the decomposition was complete, all heating was discontinued and the gaseous products of the reaction were swept from the system by means of the current of air.

The boat containing the gangue and part of the copper was withdrawn. (If copper was absent the gangue was perfectly white.) The residue was washed with dilute hydrochloric acid and warmed for a few minutes, filtered, and the filtrate was added to the main solution. The contents of the tube and the absorbers were treated as described in the general case. The main solution contained the sulphur as sulphate, the iron and the copper.

The precipitation of barium sulphate, in the presence of iron has been the subject of much discussion and experimental in-

vestigation.[9] The following method was used to eliminate the necessity of either removing or reducing the iron ions present and to prevent the occlusion of iron salts with the barium sulphate. The solution was diluted to 300–350 ccs. warmed, and ammonium hydroxide (sp. gr. 94) was added in excess. A warm dilute solution of barium chloride was added slowly and with constant stirring to this warm ammoniacal solution. Stirring was continued after the addition of the barium chloride, and hydrochloric acid was added to just acid reaction and then two ccs. excess of acid for every 300 ccs. of solution. The solution was kept hot for some time to allow the precipitate to settle. The solution was filtered through a Gooch crucible and the precipitate washed well with hot water acidulated with hydrochloric acid (two ccs. of concentrated acid per liter). The barium sulphate was dried at 120° C. and ignited at 750° C. The precipitate of barium sulphate was pure white in every case.[10]

SERIES 1

*Copper Absent*

| Weight of Mineral | Weight of $BaSO_4$ | Sulphur |
|---|---|---|
| .3562 gm. | 1.2592 gm. | 48.58% |
| .2705 gm. | .9539 gm. | 48.45% |
| .3549 gm. | 1.2490 gm. | 48.35% |
| .3643 gm. | 1.2748 gm. | 48.08% |
| .3683 gm. | 1.2847 gm. | 47.93% |
| .3200 gm. | 1.1354 gm. | 48.75% |

SERIES 2

*Copper Present*

| | | |
|---|---|---|
| .3539 gm. | 1.1841 gm. | 42.09% |
| .3129 gm. | .9644 gm. | 42.32% |
| .2560 gm. | .8012 gm. | 43.00% |

The variation in these results is due to the rapid alteration of the finely divided mineral by air oxidation. It is a well-known fact that Pyrite undergoes surface oxidation. This may be

[9] Pattison, J. Soc. Ch. Ind. 24; 7 (1905). Kuster and Thiel, Z. anorg. Ch. 22; 424 (1900).

[10] This method for the precipitation of pure barium sulphate in the presence of iron has been tested by seven competent analysts in this laboratory, who have applied this procedure to the successful estimation of the sulphur content of pyrite, marcasite, pyrrhotite, arsenopyrite, and Mohr's salt.

easily shown by heating the mineral in water, filtering and testing the filtrate for iron and sulphur as sulphate.[11]

### *Chalcopyrite*

In the analysis of chalcopyrite the carbon tetrachloride was not heated, but it was allowed to become warm, not above 40° C., during the course of the analysis from the radiation of the burners. The mineral was not heated for at least fifteen minutes as the hot gases will start the reaction. After the first action ceased, the temperature was increased to 150-175° C. for a second fifteen minute period. The temperature was again raised so that the ferric chloride just sublimed out of the boat. For the last ten to fifteen minutes the temperature was increased to 420-430° C. so that a small part of the copper chloride sublimed. The material in the boat must not fuse. The time of the reaction for a three-tenth gram sample was fifty to sixty minutes.

The volatile chlorides were washed into the main solution. The gangue and the remainder of the copper were in the boat. The contents of the boat were washed into a beaker and the solution was acidulated with hydrochloric acid. All dissolved except the gangue, which was filtered out and if the mineral was argentiferous, the gangue was examined for silver chloride. The filtrate was added to the main solution, which was analyzed for the sulphur content according to the method described under pyrite.

| Weight of Mineral | Weight of $BaSO_4$ | Sulphur |
|---|---|---|
| .3072 gm. | .7461 gm. | 33.37% |
| .3025 gm. | .7352 gm. | 33.39% |
| .3019 gm. | .7342 gm. | 33.41% |
| .3044 gm. | .7387 gm. | 33.34% |
| Average | | 33.38% |

### *Cinnabar*

The weighed sample of the mineral was warmed at 250-300° C. for ten to fifteen minutes so that the mercuric chloride produced

[11] Dana, *Textbook of Mineralogy*, Third Edition, Wiley & Sons, 1922, p. 377. Clark, *The Data of Geochemistry;* Bulletin 770, U. S. Geological Survey, p. 338 and note to this reference. Cleavland, *Elementary Treatise on Mineralogy and Geology;* First Edition 1816, p. 478 *et seq*

just sublimed out of the boat. The temperature was slowly increased to 400–450° C. and heating continued until nothing further volatilized. When the mineral was bituminous, the gangue was black in color. The time required for decomposition was thirty-five to forty minutes.

The solutions and the volatile chlorides were treated as described in the general procedure.

| Weight of Mineral | Weight of $BaSO_4$ | Sulphur |
|---|---|---|
| .5268 gm. | .4879 gm. | 12.72% |
| .5837 gm. | .5339 gm. | 12.57% |
| .5239 gm. | .4797 gm. | 12.59% |
| .5819 gm. | .5330 gm. | 12.57% |
| Average | | 12.61% |

*Bismuthinite*

The method of decomposing this mineral was very similar to that of cinnabar. The mineral was warmed at 200–250°C. for ten to fifteen minutes so that the bismuth chloride just sublimed out of the boat. The temperature was gradually raised to 450–500° C. which removed all of the bismuth and almost all of the copper which is often present in this mineral. An elevated temperature was necessary for a complete decomposition, as this mineral was mixed with cassiterite. The gangue consisted of the silicia and the cassiterite, which were unaffected by this treatment.

The volatile chlorides and the contents of the absorption flasks were treated as directed. In this instance, however, sufficient hydrochloric acid must be present to prevent the hydrolysis of the bismuth chloride. If the bismuth was allowed to hydrolyze and the product filtered off, there was danger of loss of sulfuric acid as a basic sulphate. On the other hand, the concentration of the hydrochloric acid necessary to prevent hydrolysis was too strong to permit complete precipitation of the barium sulphate. Accordingly, pure zinc was added to the acid solution which precipitated the bismuth and copper. The precipitated metals were filtered off, the excess acid was expelled and the sulphur precipitated as barium sulphate.

| Weight of Mineral | Weight of $BaSO_4$ | Sulphur |
|---|---|---|
| .5371 gm. | .1016 gm. | 2.59% |
| .7860 gm. | .1398 gm. | 2.44% |
| .9193 gm. | .1709 gm. | 2.56% |
| .7401 gm. | .1340 gm. | 2.48% |
| .9315 gm. | .1662 gm. | 2.45% |
| Average | | 2.51% |

## The Analysis of Artificial Sulphides

### *Copper Matte*

The conditions for the decomposition and the analysis of copper matte were identical with those described for the mineral chalcopyrite. (q. v.)

| Weight of Matte | Weight of $BaSO_4$ | Sulphur |
|---|---|---|
| .3068 gm. | .5036 gm. | 22.22% |
| .3112 gm. | .5053 gm. | 22.31% |
| .3132 gm. | .5089 gm. | 22.32% |
| .3012 gm. | .4898 gm. | 22.34% |
| Average | | 22.30% |

### *Nickel Matte*

The sample was heated for fifteen minutes at 300–350° C. after which the temperature was increased to 480–510° C. and kept there for twenty minutes. The time of decomposition was thirty-five to forty minutes. All of the chlorides of iron, arsenic, and antimony sublimed out of the boat and part of the copper and nickel. The chlorides of cobalt, silver and lead, the remainder of the copper and nickel, and the gangue, remained in the boat. The soluble residue in the boat dissolved readily in warm water acidulated with hydrochloric acid. It was not advisable to add this filtrate to the main solution until after the sulphur had been removed as barium sulphate. The main solution which contained the volatile chlorides was treated exactly as directed for pyrite (q. v.) for the removal of barium sulphate in the presence of iron. A pure white precipitate of barium sulphate was obtained in each case.

| Weight of Matte | Weight of $BaSO_4$ | Sulphur |
|---|---|---|
| .5788 gm. | .2972 gm. | 7.05% |
| .5527 gm. | .2803 gm. | 6.96% |
| .4710 gm. | .2402 gm. | 7.01% |
| .4571 gm. | .2331 gm. | 7.01% |
| Average | | 7.01% |

Since such success was attained in the decomposition and the analysis of these sulphides, it was thought that the process might be applied to artificial sulphides whose sulphur content was difficult to determine by ordinary methods. The determination of the sulphur content of palladium sulphide offers a difficult analytical problem. Accordingly an attempt was made to decompose this compound by the process outlined.

### *Palladium Sulphide*

Palladammonium chloride was dissolved in hot water, acidulated with hydrochloric acid and the palladium precipitated with pure zinc. The metal was filtered, washed thoroughly, and digested on the water bath with nitric acid and a little hydrochloric acid. The acid solution was evaporated to dryness several times with hydrochloric acid to expel all traces of nitric acid. The palladous chloride was taken up in water and hydrochloric acid, and palladous iodide was precipitated from it in three fractions. The middle fraction was filtered and washed thoroughly with hot water, dried at 110° C. and ignited to metal. This metal was dissolved in nitric acid and a little hydrochloric acid and converted to the chloride by repeated evaporations with hydrochloric acid.

The palladous chloride was treated with an excess of ammonia, warmed, and filtered from a very slight undissolved residue. Hydrochloric acid in slight excess was added to this strongly ammoniacal solution, which was allowed to cool and to stand for thirty-six hours. The yellow precipitate of palladosammine chloride was filtered, washed repeatedly with dilute hydrochloric acid and twice with a few ccs. of cold water and dried at 105° C. This yellow salt was converted to palladium sulphide by heating it in a stream of hydrogen sulphide which was generated from stibnite and hydrochloric acid.

The palladium sulphide was analyzed for the sulphur content.

The artificial sulphide was heated for one hour and twenty minutes at a temperature of 550° C. Almost all of the palladium chloride sublimed out of the boat at the end of this period. However, it was necessary to continue heating for a twenty

minute period at 575–600° C. Under no circumstances at any time during the decomposition was the palladous chloride in the boat allowed to fuse. When this happened, the undecomposed sulphide was held in the fused material and in this state it was practically impossible to sublime it. At the end of the two periods of heating which must not be under one hour and thirty minutes for a two-tenths gram sample, the reaction was complete and the system was allowed to cool. At the end of this time, all of the sulphide was decomposed and there was no need to sublime all of the palladium chloride from the boat.

All of the palladium chloride remained in the decomposition tube and traces in the boat. This was washed into a beaker with hot water acidulated with hydrochloric acid. No trace of palladium was detected in the first absorption tube. The contents of the absorption tube were treated and analyzed exactly as described under the general case.

| Weight of Sample | Weight of $BaSO_4$ | Sulphur |
|---|---|---|
| .2011 gm. | .3380 gm. | 23.09% |
| .2027 gm. | .3422 gm. | 23.19% |
| Average | | 23.14% |
| Calculated per cent. Sulphur | | 23.10% |

### The General Procedure for the Analysis of Selenides

The apparatus used for the decomposition and analysis of the selenides was essentially the same as that described for the sulphides. Only one absorber was used and this contained 60 ccs. of 1 : 1 hydrochloric acid. Tests were made with several absorbers and with different absorbing materials, but in each case no trace of selenium was found beyond the first bottle.

The mineral was decomposed in the same general manner as the sulphide minerals. The volatile material was washed into the beaker which contained the washings from the absorber. This solution was boiled to reduce the selenic acid to selenious acid after which it was diluted to 250 ccs. and the selenium precipitated with sulphur dioxide. The solution was boiled to convert selenium to the black variety, which was filtered on a Gooch crucible, washed well with water and then with alcohol, dried at 105° C. and weighed.

In all other respects the appartus and the procedure were the same as reported for the sulphides.

### *Berzelianite in Calcite*

The mineral was not heated for the first ten minutes, in order that the hot gases might start the reaction. After this reaction commenced, the temperature was gradually raised to 250–300° C. and kept there for a second ten minutes period. To complete the decomposition, the mineral was heated at 375–425° C. for a third ten minute period. This gradual increase of temperature was necessary because the material was disseminated through calcite, the gangue material, which tended to retard the decomposition. The time required for the decomposition was thirty-five to forty minutes.

When the reaction was completed the volatile material in the tube was washed into the beaker which held the washings of the absorber. This solution was analyzed for selenium.

| Weight of Material | Weight of Selenium | Selenium |
|---|---|---|
| .2520 gm. | .0078 gm. | 3.09% |
| .2512 gm. | .0079 gm. | 3.14% |
| .2616 gm. | .0082 gm. | 3.13% |
| .3024 gm. | .0096 gm. | 3.17% |
| Average | | 3.13% |

### *Zorgite*

The mineral was heated at 200° C. for ten to fifteen minutes after which the temperature was increased to 400–450° C. for fifteen to twenty minutes. The time of the decomposition was thirty-five minutes for a quarter gram sample.

The contents of the tube were added to the washings of the absorber and from this solution the selenium was precipitated.

The boat contained the major portion of the copper, the silver chloride and the gangue. The contents of the boat were leached with warm water acidulated with hydrochloric acid. The copper chloride was filtered from the silver chloride and the gangue. The filtrate was added to the main solution after the selenium was precipitated.

| Weight of Material | Weight of Selenium | Selenium |
|---|---|---|
| .3743 gm. | .1060 gm. | 28.32% |
| .2577 gm. | .0729 gm. | 28.29% |
| .2911 gm. | .0828 gm. | 28.44% |
| .2579 gm. | .0733 gm. | 28.42% |
| Average | | 28.37% |

### The Procedure for the Analysis of a Telluride

*Altaite in Calcite*

The procedure for the decomposition and analysis of the mineral was very similar to that which was used for the selenides. The burner at *K* was not used and the absorbing material was 60 ccs. of dilute (1:4) hydrochloric acid; these were the only differences from the procedure described.

The mineral was heated for thirty minutes, at a temperature of 250–275° C. The volatile material in the decomposition tube was washed with dilute (1:5) hydrochloric acid into the beaker containing the washings of the absorber. The solution was boiled to reduce the telluric acid to tellurous acid, diluted to 250 ccs. and from it the tellurium was precipitated with sulphur dioxide. The precipitate was filtered on a Gooch crucible washed with water and then with alcohol, dried at 105° C. cooled and weighed.

The material in the boat consisted of the silica, lead chloride and the calcite, part of which was transposed to the chloride.

| Weight of Material | Weight of Tellurium | Tellurium |
|---|---|---|
| .3567 gm. | .0159 gm. | 4.48% |
| .3106 gm. | .0141 gm. | 4.57% |
| .3378 gm. | .0153 gm. | 4.53% |
| Average | | 4.53% |

The minerals, pyrrhotite, marcasite, arsenopyrite, stibnite, tetrahedrite, cobaltite, molybdenite, galena, enargite, sylvanite, and tiemannite were completely decomposed when treated with an air carbon tetrachloride mixture, as previously described, but no quantitative determinations were made of their sulphur or selenium content.

### Conclusions

1. A method for the detection and removal of traces of sulphur or sulphur compounds from carbon tetrachloride is described.

2. A mixture of air and carbon tetrachloride vapor is shown to be a convenient and satisfactory reagent for the complete decomposition and chlorination of natural and artificial sulphides at elevated temperatures.

3. Decomposition of the sulphides, sphalerite, pyrite, cinnabar, bismuthinite, chalcopyrite, nickel matte, copper matte, and palladium sulphide, by an air carbon tetrachloride vapor mixture at elevated temperatures provides a rapid and convenient means of oxidizing the sulphur content of these bodies prior to the quantitative estimation of the sulphur.

4. The selenium and tellurium bearing minerals, berzelianite, zorgite, and altaite may be completely decomposed and the selenium and tellurium content prepared for quantitative estimation by decomposing in a stream of air and carbon tetrachloride at elevated temperatures.

5. A method is described for the precipitation of pure barium sulphate in the presence of certain metallic ions forming hydroxides insoluble in excess of ammonium hydroxide.